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Anomalous Energy Effects in Some Aliphatic and Alicyclic Aza Systems and Their Nitro Derivatives

Jane S. Murray, Paul C. Redfern, Jorge M. Seminario, and Peter Politzer*

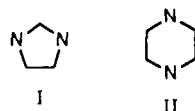
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We have used an ab initio SCF molecular orbital approach in conjunction with the isodesmic reaction procedure to investigate anomalous energy effects in aliphatic and alicyclic aza systems. These molecules are found to be significantly stabilized, which we attribute to σ -conjugation of the nitrogen lone pairs; these are presumably delocalized to some extent through the σ -bond framework. The stabilization increases with the number of nitrogens in a series of similar molecules and is greater in cyclic systems, particularly when rings are fused. The magnitudes of the most negative electrostatic potentials of the aza nitrogens, which can be viewed as indicating the degrees of delocalization of the nitrogen lone pairs, decrease as the added stability increases. In these systems, the introduction of nitro groups also has an overall stabilizing effect, which may be due to further delocalization of σ -electrons, reflecting the strong electron-withdrawing power of the nitro group.

Introduction

In a recent computational study,¹ we have used the well-established isodesmic reaction procedure^{2,3} to show that the presence of the nitrogens in the diaza acyclic imidazoline (I) and piperazine (II) rings confers an added degree of stability to these molecules.

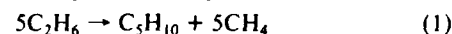


We attributed this to σ -conjugation of the nitrogen lone pairs.^{4,5}

We now show that this is a general effect that applies to a large group of aliphatic and alicyclic aza systems and is even amplified by the presence of nitro substituents. These stabilizing tendencies are of particular interest because of the importance of many of these molecules as high-energy systems.

Methods and Procedure


The isodesmic reaction procedure^{2,3} is a means of studying anomalous energy effects in molecules. An isodesmic reaction is a hypothetical chemical process in which the number of bonds of each formal type remains the same on each side of the equation, but their mutual relationships are changed. Representative isodesmic reactions for cyclopentane (C_5H_{10}) and imidazolidine ($C_3N_2H_8$) are given in eqs 1 and 2, respectively. The ΔE values



for reactions such as these reveal any deviations from bond energy additivity and are therefore interpreted as being due to special energy effects associated with the molecule being investigated,

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TABLE I: Comparison of Isodesmic Reaction Energies Obtained at Various Computational Levels

molecule	$\Delta E_{\text{isodesmic}}^a$ kcal/mol		
	3-21G	6-31G* ^b	MP2/6-31G* ^c
CH ₃ CH ₂ CH ₃	-1.4	-0.8	-2.2
NH(CH ₃) ₂	-2.3	-2.2	-4.1
CH ₃ CH ₂ NO ₂	-7.2	-3.5	-5.0
NH ₂ CH ₂ NH ₂	-10.5	-7.9	-10.1
	-11.3	-9.0	-16.8

^a Reaction energies are obtained from energies of the reactant and product molecules optimized at the respective computational levels.

^b The total energies of these molecules, in the order listed, are -118.263 65, -134.238 85, -282.701 02, -150.237 11, and -227.128 11 hartrees. ^c The total energies of these molecules, in the order listed, are -118.674 41, -134.678 10, -283.520 21, -150.707 91, and -227.862 69 hartrees.

e.g., strain, resonance stabilization, steric effects, etc. ($\Delta E < 0$ indicates the presence of stabilizing factors, while $\Delta E > 0$ implies destabilization.)

We have used the ab initio self-consistent-field (SCF) molecular orbital approach (GAUSSIAN88⁶) to optimize molecular geometries and obtain their energies at the 3-21G level. SCF methods have been shown to give satisfactory results for isodesmic energy differences,^{3,7} when viewed on a relative basis.

As part of our analysis, we have computed the electrostatic potentials in the neighborhoods of the aza nitrogens in some of the molecules studied. The electrostatic potential $V(\vec{r})$ that is created at any point \vec{r} in the space around a molecule by its nuclei and electrons is given rigorously by eq 3. Z_A is the charge on nucleus A , located at \vec{R}_A , and $\rho(\vec{r})$ is the electronic density function of the molecule, which we obtain from the molecular wave function.











$$V(\vec{r}) = \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' \quad (3)$$

$V(\vec{r})$ is a real physical property that can be determined experimentally as well as computationally⁸ and is well established as a means of interpreting and predicting chemical reactive behavior, especially toward electrophiles.⁸⁻¹⁰ In the present work, however, we use it as an indication of the degrees of delocalization of nitrogen lone pairs. Following up on earlier work,¹¹ we shall also use the position of the most negative value of the potential as a means for defining dihedral angles involving the nitrogen lone pairs. We have computed $V(\vec{r})$ at the STO-5G level, using the 3-21G optimized structures. Extensive investigations have shown that ab initio SCF approaches produce generally reliable representations of $V(\vec{r})$;^{9,12-14} in particular, we have had good experience with the STO-5G basis set.

Results

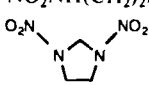
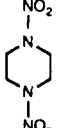
In order to investigate the dependence of isodesmic reaction energies upon the computational level, we have carried out a

TABLE II: Calculated 3-21G Molecular Energies and Isodesmic Reaction Energies

molecule	total energy, hartrees	$\Delta E_{\text{isodesmic}}^a$ kcal/mol	
		$\Delta E_{\text{isodesmic}}^a$	relative $\Delta E_{\text{isodesmic}}^a$
CH ₄	-39.976 88	0.0	c
NH ₃	-55.872 20	0.0	c
C ₂ H ₆	-78.793 95	0.0	c
CH ₃ NH ₂	-94.681 66	0.0	c
C ₃ H ₈	-117.613 30	-1.4	0.0
NH(CH ₃) ₂	-133.494 85	-2.3	-0.9
NH ₂ CH ₂ NH ₂	-149.403 12	-10.5	-9.1
NH ₂ (CH ₂) ₂ NH ₂	-188.217 57	-8.8	c
NH ₂ CH ₂ NHCH ₃	-188.213 67	-11.2	c
III ^b 	-194.080 55	+3.0	0.0
IV 	-209.974 53	-5.7	-8.7
I ^b 	-225.863 61	-11.3	-14.3
V ^b 	-232.916 91	-9.1	0.0
VI 	-248.803 26	-13.0	-3.9
II ^b 	-264.689 25	-16.7	-7.6
VII 	-264.694 57	-20.1	-11.0
VIII 	-303.505 64	-16.3	c
IX 	-372.962 58	-41.1	c
X 	-450.602 21	-44.5	c

^a Relative isodesmic energies are referred to the corresponding hydrocarbon. ^b Data are taken from ref 1. ^c Not applicable.

TABLE III: Calculated 3-21G Molecular Energies and Isodesmic Reaction Energies for Some Nitro Derivatives

molecule	total energy, hartrees	$\Delta E_{\text{isodesmic}}^a$ kcal/mol	
		$\Delta E_{\text{isodesmic}}^a$	relative $\Delta E_{\text{isodesmic}}^a$
CH ₃ NO ₂	-242.255 85	0.0	
NH ₂ NO ₂	-258.138 00	0.0	
CH ₃ CH ₂ NO ₂	-281.084 40	-7.2	
(CH ₃) ₂ NNO ₂	-335.774 89	-11.3	
NO ₂ NH(CH ₂) ₂ NHNO ₂	-592.756 41	-13.1	
XI 	-630.413 58	-22.9	
XII 	-669.244 36	-31.4	

comparison of 3-21G, 6-31G*, and MP2/6-31G* results for a limited number of systems. MP2/6-31G* geometry optimizations for nitroethane and imidazolidine were carried out using the Cambridge Analytic Derivatives Package (CADPAC)¹⁵ at the San Diego Supercomputer Center; GAUSSIAN88⁶ was used for all other computations. Our results are given in Table I. For each of these three computational approaches, the ΔE values show the same trend, becoming more negative in going from propane to imida-

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zolidine. These data indicate that isodesmic reaction energies computed at different levels will lead to similar conclusions regarding anomalous energy effects when viewed on a relative basis. For the present study we have chosen the 3-21G approach as being computationally the most practical.

Our calculated 3-21G molecular and isodesmic reaction energies for a group of aliphatic and alicyclic systems and some of their nitro derivatives are presented in Tables II and III, respectively. Positive ΔE values are commonly interpreted as indicating strain. For example, the 3-21G isodesmic reaction energy of cyclopropane is 31 kcal/mol,¹⁶ which is quite close to its widely quoted strain energy of 27 kcal/mol.¹⁷ The ΔE value of cyclopentane, +3 kcal/mol (Table II), indicates a low degree of strain, in agreement with its reported strain energy of 7 kcal/mol.¹⁷ All other molecules in Table II have negative isodesmic energies, reflecting varying degrees of stabilization, which we attribute to σ -conjugation.^{4,5}

Looking first at Table II, it is important to note that the saturated unstrained hydrocarbons propane and cyclohexane have small negative calculated ΔE values. These results are consistent with theoretical studies that have shown that a stabilizing delocalization of σ -electrons occurs in saturated hydrocarbons.^{18,19} The aza systems have more negative ΔE 's than their hydrocarbon analogues, presumably reflecting the additional presence of nitrogen lone pairs that are delocalized to some degree through the σ -bond framework. This extra stabilization occurs to a greater extent in the cyclic than in the noncyclic systems and increases even more strikingly when there are fused rings. Within any particular aliphatic or alicyclic series of molecules with the same number of first-row atoms, the stabilization is greater as the number of nitrogens increases. This point is brought out even more strikingly by the relative $\Delta E_{\text{isodesmic}}$ values that are given in Table II.

It is interesting to observe that the 1,3-diaza systems show a greater degree of stabilization than do their 1,4-diaza isomers. This can be seen in the ΔE values for the pair $\text{NH}_2\text{CH}_2\text{NHCH}_3$ and $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ and again for 1,3- and 1,4-diazacyclohexane (VII and II) [Table II]. The fact that the fused-ring systems IX and X have large calculated ΔE values (significantly more than twice the ΔE 's of I and II) may be due to the additional two 1,3-diaza groupings that occur in each by virtue of being fused.

Isodesmic reaction energies for nitro derivatives of ethane, dimethylamine, 1,2-diaminoethane, imidazoline, and piperazine are listed in Table III. The ΔE values for these nitro systems are larger in magnitude than those for the corresponding unsubstituted molecules, indicating that the introduction of nitro groups has an overall stabilizing effect upon these systems. This additional stabilization may be due to enhanced delocalization of the σ -electrons, particularly the amine lone pairs, resulting from the strong electron-withdrawing power of the nitro group. (Nitro groups do not invariably have a stabilizing effect; when substituted on tertiary carbons in strained molecules, they are found to destabilize the systems.²⁰)

Discussion

We have suggested that the extra stability provided by the replacement of carbons by nitrogens in aza aliphatic and alicyclic systems, such as those in Table II, is largely due to lone-pair σ -conjugation. As a measure of the extent of this conjugation, we examine the electrostatic potentials $V(\vec{r})$ in the vicinities of the aza nitrogens.

$V(\vec{r})$ for aliphatic and aromatic amines,^{1,21-26} hydrazines,¹¹ and

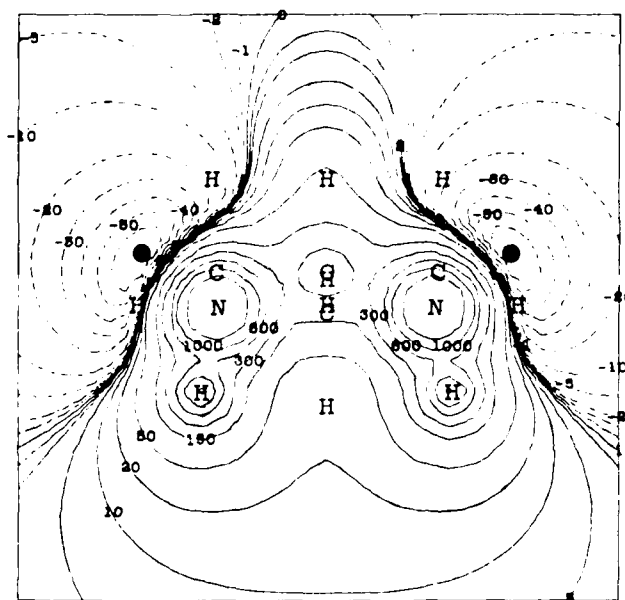


Figure 1. Calculated electrostatic potential of 1,3-diazacyclohexane (VII), in kilocalories per mole, in a plane passing through the two NH groups. The projections of other nuclear positions are shown by their atomic symbols. Dashed contours correspond to negative potentials. The positions of the most negative potentials are indicated; the value is (●) -72.0.

TABLE IV: Calculated Electrostatic Potential Minima [$V_{\text{min}}(\text{N})$] of Aza Nitrogens

	molecule	$V_{\text{min}}(\text{N})$, kcal/mol
	NH_3	-109.3 ^a
	$\text{NH}(\text{CH}_3)_2$	-100.0
IV		-97.2
VI		-95.5
I		-95.3 ^b
II		-93.8 ^b
VII		-93.5
VIII		-88.9
IX		-88.2 (N) -86.0 (N')
X		-98.5 (N) -88.9 (N')

^a The $V_{\text{min}}(\text{N})$ for NH_3 is taken from ref 24. ^b The $V_{\text{min}}(\text{N})$ data for imidazoline and piperazine are taken from ref 1.

nitrogen-containing heterocycles^{10,27,28} are largely dominated by strong negative regions attributed to the nitrogen lone pairs, indicative of sites attractive to electrophiles. An example of these characteristic potentials is given by the $V(\vec{r})$ of 1,3-diazacyclo-

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hexane (VII), shown in Figure 1; each ring nitrogen has a negative potential region with a most negative value, $V_{\min}(\text{N})$, associated with it. The $V_{\min}(\text{N})$ values for VII and various other aza systems are listed in Table IV. [$V_{\min}(\text{N})$ for VII is not located in the plane shown in Figure 1.]

In an earlier study, we have shown that the $V_{\min}(\text{N})$ values of $\text{NH}_2\text{-X}$ molecules reflect the total electron-attracting tendencies of the substituents X.²⁴ The decrease in magnitude of $V_{\min}(\text{N})$ relative to NH_3 is viewed as an indication of the degree to which the nitrogen lone pair electronic density is redistributed or "delocalized" throughout the remainder of the molecule. We interpret the $V_{\min}(\text{N})$ values in Table IV in a similar manner.

In general, these $V_{\min}(\text{N})$ decrease in magnitude as the isodesmic reaction energies of the corresponding molecules become more negative. (This trend holds rigorously within the five- and six-membered cyclic systems taken separately.) Thus, increased delocalization of the nitrogen lone pairs, as measured by decreases in the magnitudes of the $V_{\min}(\text{N})$ values, roughly parallels an increase in stability. These data support the view that the enhanced stability in aliphatic and alicyclic aza systems is linked to lone-pair σ -conjugation.

It has been pointed out that the 1,3-diaza molecules, $\text{NH}_2\text{C-H}_2\text{NHCH}_3$ and 1,3-diazacyclohexane, have a greater degree of stabilization than their 1,4-diaza isomers (Table II). We suggest that this extra stabilization comes about because these systems can assume conformations that permit the σ -delocalization of each nitrogen lone pair to reinforce that of the other. The tendency to assume such geometries has been noted and studied earlier^{4,29-31} and has been called the anomeric effect. It is found in $\text{R}'\text{-X-C-Y-R}$ systems, where X and Y are heteroatoms with lone pairs, that the dihedral angle defined by the lone pair of X and the X, C, and Y nuclei tends to be close to 180° . This has been rationalized in the molecular orbital framework as stabilization occurring via delocalization of electronic density from a non-bonding molecular orbital of X into the σ^* -orbital of the adjacent C-Y bond.^{30,31}

Recent ab initio 3-21G calculations of $\text{NH}_2\text{CH}_2\text{NH}_2$, the smallest molecule containing the 1,3-diaza moiety, have reported that its most stable conformer possesses a calculated structure consistent with the anomeric effect;³² the lone-pair-N-C-N dihedral angles are 180° . (We have included $\text{NH}_2\text{CH}_2\text{NH}_2$ in Tables I and II.) The 1,3-diaza rings I, VII, and VIII contain this methylenediamine unit and have calculated $V_{\min}(\text{N})\text{-N-C-N}$ dihedral angles that increase from 129° in I to 169° in VII to 174° in VIII. This is paralleled by a decrease in the N-C bond distances within the N-C-N groupings of I, VII, and VIII; these are 1.486, 1.468, and 1.459 Å, respectively. These data are consistent with the delocalization of the nitrogen lone pairs increasing as the structural criteria for the anomeric effect are more fully satisfied. It is interesting to note that the $V_{\min}(\text{N})$ values decrease in magnitude in the same direction, from the five- to the seven-membered 1,3-diaza rings, which is also consistent with increased nitrogen lone pair σ -conjugation. That the $V_{\min}(\text{N})\text{-N-C-N}$ dihedral angles in I deviate significantly from 180° may be a result of a lack of flexibility in the imidazolidine ring, which prevents a more preferred conformation with regard to the position of the nitrogen lone pairs and the adjacent C-N bonds.

We find that the most stable conformers of the fused ring systems, IX and X, have geometries that preclude the anomeric effect from operating in both directions within their respective

1,3-diaza groupings. For example, our calculated $V_{\min}(\text{N}')\text{-N'-C-N}$ and $V_{\min}(\text{N})\text{-N-C-N'}$ dihedral angles in X are 176° and 61° , respectively. Furthermore, the $V_{\min}(\text{N}')$ and the N'-C bond distances (-88.9 kcal/mol and 1.455 Å) are smaller in magnitude than the $V_{\min}(\text{N})$ and the N-C bond distances (-98.5 kcal/mol and 1.469 Å). These data are consistent with lone-pair σ -conjugation occurring to a greater extent for the nitrogens, designated as N' in Table IV, which can assume conformations that closely satisfy the requirements for the anomeric effect. A similar situation is observed for the fused five-membered ring system, IX, which has four 1,3-diaza groupings in succession around the outer framework of the molecule. In one direction around the ring, the $V_{\min}(\text{N})\text{-N-C-N}$ dihedral angles are 150° or 151° ; in the opposite direction, these angles are alternately 83° and 26° . That each nitrogen in IX satisfies the anomeric effect criterion in one direction is reflected in the similar $V_{\min}(\text{N})$ and $V_{\min}(\text{N}')$ values (Table IV).

Stabilization due to ring nitrogens in alicyclic systems may be a key factor involved in understanding some of the anomalies in the thermolysis patterns of nitramines. It has been found in the fast thermolysis of many secondary nitramines that the relative initial concentration of NO_2 depends qualitatively on the N-N bond distance and the average asymmetric stretching frequency of $-\text{NO}_2$ [$\nu_{\text{as}}(\text{NO}_2)$].³³ Molecules with long N-N bonds and high $\nu_{\text{as}}(\text{NO}_2)$ values are often strong liberators of NO_2 upon fast thermolysis; those with short N-N bonds and low stretching frequencies often do not liberate NO_2 or do so in competition with other reactions. 1,3-Dinitroimidazolidine (XI) deviates from this qualitative trend; it has a relatively short calculated N-N bond length (1.344 Å)¹ but liberates NO_2 by cleavage of the N-N bond during thermolysis.³³ This exceptional behavior is believed to reflect an anomalously high stability of the imidazolidine ring,³⁴ consistent with the stabilization shown for this molecule in Table II.

Summary

The isodesmic reaction procedure has been used to study the effect of replacing carbons by nitrogens in a group of aliphatic and alicyclic systems. In all instances, we find the aza systems to possess significant degrees of added stability, which we attribute to σ -conjugation. This presumably involves the nitrogen lone pairs, which are delocalized to some extent through the σ -bond framework. The stabilization due to the presence of nitrogens is greater in cyclic systems, particularly when rings are fused, and it increases with the number of nitrogens. Decreases in the magnitude of the most negative electrostatic potentials of the nitrogens, which can be viewed as a measure of increasing delocalization of the nitrogen lone pairs, roughly parallel the increase in stability. Isodesmic reaction energies for nitro derivatives indicate that in these systems the introduction of nitro groups also has an overall stabilizing effect, which may be a consequence of further delocalization of σ -electrons, particularly the amine lone pairs, due to the strong electron-withdrawing effect of the nitro group.

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Registry No. IV, 123-75-1; VI, 110-89-4; VII, 505-21-5; VIII, 7092-43-5; IX, 124855-09-0; X, 5409-42-7; XI, 5754-91-6; XII, 4164-37-8; $\text{CH}_3\text{CH}_2\text{CH}_3$, 74-98-6; NHMe_2 , 124-40-3; $\text{CH}_3\text{CH}_2\text{NO}_2$, 79-24-3; $\text{CH}_3(\text{NH}_2)_2$, 2372-88-5; CH_4 , 74-82-8; NH_3 , 7664-41-7; H_3CCH_3 , 74-84-0; MeNH_2 , 74-89-5; $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, 107-15-3; $\text{NH}_2\text{CH}_2\text{NHMe}$, 123105-11-3; MeNO_2 , 75-52-5; NH_2NO_2 , 7782-94-7; Me_2NNO_2 , 4164-28-7; $\text{NO}_2\text{NHCH}_2\text{CH}_2\text{NHNO}_2$, 505-71-5.

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